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EFFECT OF BOTTOM SEDIMENT CONTINUING HYDROGEN SULFIDE ON MATERIALS, PART I

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ABSTRACT

Plastic, synthetic ropes, natural fiber ropes, electrical cable insulations, and a wood panel were partially exposed in the black, bottom sediment of Port Hueneme Harbor to determine the effect of hydrogen sulfide on materials. After one year of exposure, the materials were recovered and examined for fouling and biodeterioration. In addition, hardness and moisture absorption tests were conducted on the plastic panels while tensile strength tests were conducted on rope specimens. Significant changes in hardness and moisture absorption were registered by nylon and phenolic laminate plastics. Decrease in tensile strength was experienced by all of the synthetic rope specimens. The natural rope specimens were totally destroyed by marine organisms. The wood panel was riddled by marine borers.

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Plastic, synthetic ropes, natural fiber ropes, electrical cable, insulations, and a wood panel were partially exposed in the black, bottom sediment of Port Hueneme Harbor to determine the effect of hydrogen sulfide on materials. After one year of exposure, the materials were recovered and examined for fouling and biodeterioration. In addition, hardness and moisture absorption tests were conducted on the plastic panels while tensile strength tests were conducted on rope specimens. Significant changes in hardness and moisture absorption were registered by nylon and phenolic laminate plastics. Decrease in tensile strength was experienced by all of the synthetic rope specimens. The natural rope specimens were totally destroyed by marine organisms. The wood panel was riddled by marine borers.

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Marine borers						
Aquatic animals						
Plastics						
Rope						
Wood						

INTRODUCTION

An anaerobic environment devoid of oxygen and where marine sulfate-reducing bacteria flourish and produce hydrogen sulfide is found in many parts of the world's oceans. These areas are usually found in places where circulation of oxygenated seawater is restricted or reduced such as in harbors and bays (especially in bottom mud) and in basins (bottom waters of the Black Sea). In an anaerobic environment, the sulfate-reducing bacteria utilize sulfates and sulfites in the absence of oxygen during their metabolic process leading to the formation of hydrogen sulfide (rotten egg smell). The anaerobic corrosion of metals exposed in such an environment is widespread and destructive. For example, it is reported that extensive corrosion and deterioration is experienced by pipes, pumps, storage tanks, steel pilings in harbors, mooring chains of buoys, ship hulls, and painted surfaces of metals in such an environment.[1,2,3]

To obtain additional knowledge about what will happen to materials exposed in bottom sediments containing hydrogen sulfide, materials other than metals were exposed in the bottom mud. Reported herein are the test results obtained on various plastic materials, synthetic and natural fiber ropes, electrical cable insulating materials, and a Douglas fir panel which had been exposed in the bottom sediment of Port Hueneme Harbor for a period of one year.

MATERIALS AND METHOD

For the long-term exposure tests in the bottom sediments containing hydrogen sulfide, 6x12 inch plastic specimens of varied thicknesses were placed in a rack as shown in Figure 1. The specimens were held in place by four molded, grooved polyethylene insulators and were separated from each other by one inch. The center divider and end plates were titanium alloy 75-A. The rods through the insulators were nickel-copper alloy 400 fastened with nuts and washers of the same composition. Polyvinyl chloride (PVC) washers were used between the metal washers and the end plates. Prior to placing the 6 x 12 inch plastic panels in the titanium rack, each specimen (listed in Table 1) was weighed and then tested for hardness with a Durometer Type D or Type A-2 in a temperature and humidity controlled room (75°F, 20%RH). Rope specimens (nylon, polypropylene, polyester, manila, and cotton) with eye-splices were placed around the titanium rack in such a way that the center section of the ropes would be embedded in the mud. The eye-splices were placed in each rope specimen

so that tensile strength tests can be conducted on the recovered ropes. Six inch long electrical cables covered with different insulating materials (butyl rubber, neoprene rubber, natural rubber, PVC, polyethylene, and TFE) were also tested by securing these to a phenolic laminated plastic plate (Figure 2). For sign of any deterioration, only visual examinations were conducted under a sterescopic microscope on the recovered cable specimens. A Douglas fir panel was also attached to the rack to determine if marine wood boring animals are present at the sediment-seawater interface.

Two titanium test racks (one rack to be exposed for one year and the second rack for a period of two years) with materials were prepared and placed in the black bottom sediment present in Port Hueneme Harbor by scuba divers (Figure 3). A shovel was used by the divers to bury the racks in the sediment because it contained a mixture of large and small rocks and debris, making it difficult to shove the racks deeply into the mud. A third rack with replicate test specimens was exposed near the surface of the water from an NCEL corrosion testing dock located inside the Port Hueneme Harbor. The rack was suspended with a synthetic rope about three feet below mean low tide from the dock. Plans are to expose this rack near the surface for a period of two years so that the effects of fouling, biodeterioration, and other changes which may occur to the test panels can be compared to those replicate panels exposed in the bottom sediments.

RESULTS AND DISCUSSION

Bottom Rack

The titanium rack with materials which has been exposed in the bottom sediment for a period of one year was recovered by divers during the month of September 1972 (Figure 4). The depth into which the materials were buried in the sediment can be determined by the end plate of the titanium rack (Figure 5). There was light fouling growth attached to the recovered materials. The sessile organisms found attached to the materials were composed mostly of encrusting bryozoa (several species), calcareous tubeworms, and rock oysters. These fouling organisms are not adversely affected by living in a seawater environment containing hydrogen sulfide and low dissolved oxygen concentration. After the plastic panels (6 x 12 inch) were cleaned of marine growth, hardness and moisture absorption tests were conducted. The results of these tests are presented in Table 1. The hardness test was conducted over two different sections of the surface of the plastic panels - the section which was buried in the mud and the section which was exposed to seawater above the mudline. The two sections would be distinguished by the discoloration present in the plastic panel. For example, the section of a PVC panel (grey)

buried in the sediment had turned to black. The hydrogen sulfide in the sediment had reacted with either the tin or the lead present in the PVC plastic panel to form tin or lead sulfide which is black. In another marine exposure test a vinyl paint (orange) containing lead had changed to black when exposed in an anaerobic environment containing hydrogen sulfide in the deep-ocean environment.[4] There was no significant difference in hardness between the two sections. It should be noted, however, that polyethylene and nylon showed a slight increase in hardness where it was exposed in seawater as compared to the section buried in the sediment. There were some differences in hardness between the unexposed (dry) and the exposed (wet) panels. For example, polyethylene, polypropylene, vinyl (pp), PVC, polystyrene, and TFE increased in hardness after being exposed in seawater. On the other hand, phenolic laminate and nylon panels decreased in hardness. The hardness of vinyl (pm) polycarbonate, acrylic, and polyurethane panels remained about the same before and after exposure in the sea.

Most of the plastic materials did not absorb significant amounts of moisture during the one year exposure in the harbor. The exceptions to this were phenolic laminate and nylon panels which absorbed significant amounts of moisture during this period.

The recovered rope specimens (nylon, polyester, polypropylene, manila, and cotton) were covered with a layer of fine silt and some encrusting bryozoans. The fibers of manila and cotton ropes were deteriorated so severely by microorganisms that the fibers could easily be torn apart by one's fingers (Figure 6 and 7). The results of a tensile strength test conducted on the recovered synthetic ropes are presented in Table 2. The tensile strength of polyester, polypropylene, and nylon ropes decreased by 6.3, 9.5, and 19.7 percent, respectively. Data on tensile strength of manila and cotton ropes were not obtained since these had been severely deteriorated by biological activity. It is of interest to note that, although the tensile strength of polypropylene ropes had decreased when exposed in the bottom sediment, it had increased when such rope specimens were exposed in the deep-ocean environment (6000-ft depth).[5]

Visual examination of the electrical cable insulations (butyl rubber, neoprene rubber, natural rubber, PVC, polyethylene, and TFE) conducted under a stereoscopic microscope showed that the surface of a natural rubber insulating material had deteriorated badly, probably due to effects of hydrogen sulfide and microorganisms (surface cracking). The other materials were in good condition. Fouling organisms which were found on the various insulating materials included encrusting and branching bryozoans, hydroids, calcareous tubeworms, and small barnacles (Figure 8).

The 1/4 x 4 x 12 inch Douglas fir panel which was exposed immediately above the bottom sediment was riddled by *Bankia* and *Teredo* (molluscan borers) and also by *Limnoria quadripunctata* and

Chelura (crustacean borers) as shown in Figure 9.

Surface Rack

The replicate test specimens in a titanium rack exposed at the surface of the water in Port Hueneme Harbor was covered with a moderately dense growth of fouling - considerably more than the rack which had been exposed in bottom sediments. Large mussels, barnacles, encrusting and branching bryozoans, tubeworms and kelps were the major fouling growths found attached to the plastic panels and rope specimens (Figure 10). Compared to the severely deteriorated condition of the cotton and manila ropes exposed at the bottom, the cotton and manila rope specimens exposed at the surface were in relatively good condition. As soon as the visual inspection was completed, the rack with the test specimens was immediately submerged in the harbor water for continued testing.

CONCLUSIONS

Biodeterioration of materials such as cotton and manila ropes (natural fibers), and wood placed exposed on the bottom sediment were severe and rapid due to the activity of microorganisms and wood borers. The synthetic fiber ropes (nylon, polypropylene, and polyester) were not affected by marine organisms but were affected by seawater in an anaerobic environment resulting in decreased tensile strength. A natural rubber electrical insulating material exposed in the bottom sediment experienced severe surface cracking, probably due to the effect of both hydrogen sulfide and microorganisms. Other insulating materials such as neoprene rubber, PVC, polyethylene, and TFE were not affected. Except for the 6 x 12 inch phenolic laminate and nylon panels, the majority of the 6 x 12 inch plastic panels were not affected significantly by the seawater - hydrogen sulfide environment found in the bottom sediments of Port Hueneme Harbor. The principal fouling organisms found attached to the test materials exposed at the bottom were encrusting bryozoans (several species), calcareous tubeworms and rock oysters.

FUTURE PLANS

The second titanium rack with replicate test panels as above, is undergoing continued exposure testing in the bottom sediment at the same location. It will be recovered after two years of exposure and the materials will be examined and evaluated for fouling attachment, biodeterioration, and other changes which may occur during this

period. The materials exposed at the surface of the water in Port Hueneme Harbor will also be examined and evaluated at the same time for comparison purposes.

Table 1. Result of Hardness and Moisture Absorption Tests or Plastic Panels

Material	Thickness (inch)	Hardness Test[1]			Moisture Absorption Test (gm)	
		Before Exposure	After Exposure In Mud	After Exposure In water	Before Exposure	After Exposure
Rigid Vinyl, Clear, PM	1/16	85.0	85.0	85.0	88.60	88.30
Polycarbonate	1/8	85.0	85.0	85.0	172.88	173.10
Acrylic, G.	1/8	90.0	90.0	91.0	159.55	161.62
Polyurethane	1/16	94.5[2]	95.0	95.0	65.25	65.58
Polyethylene	1/8	46.6	50.0	51.0	132.84	132.78
Polypropylene	1/8	74.0	78.0	78.5	134.89	134.85
Rigid Vinyl, Black, PP	1/32	Too Thin for testing			47.0	47.16
PVC	1/8	85.0	86.0	86.0	211.08	211.12
Polystyrene	1/8	82.3	84.0	84.0	129.32	129.48
TFE	1/16	55.5	62.0	62.0	103.52	103.28
Rigid Vinyl, Clear, PP	1/8	85.0	88.0	88.0	184.84	184.88
Phenolic Laminate, Grade XXX	1/8	93.0	90.5	90.0	201.28	210.31
Nylon	1/8	77.0	65.0	66.5	171.03	184.25

1. Durometer, Type D
2. Durometer, Type A-2 (for softer material)

Table 2. Result of Tensile Strength Test on Ropes (lbs)

Rope	Diam. (inch)	Before Exposure[1,2]	After Exposure[1,2]	Percent Change
Polyester	1/4	1533	1437	6.3 decrease
Polypropylene	1/4	1137	1029	9.5 decrease
Nylon	1/4	1514	1215	19.7 decrease
Manila[3]	1/4	701	Biodegradated	
Cotton	1/2	1646	Biodegradated	

1. Average of 2 ropes
2. Tensile strength applied at 3 inch per minute
3. Type M, Class 2. Mildew Resistent

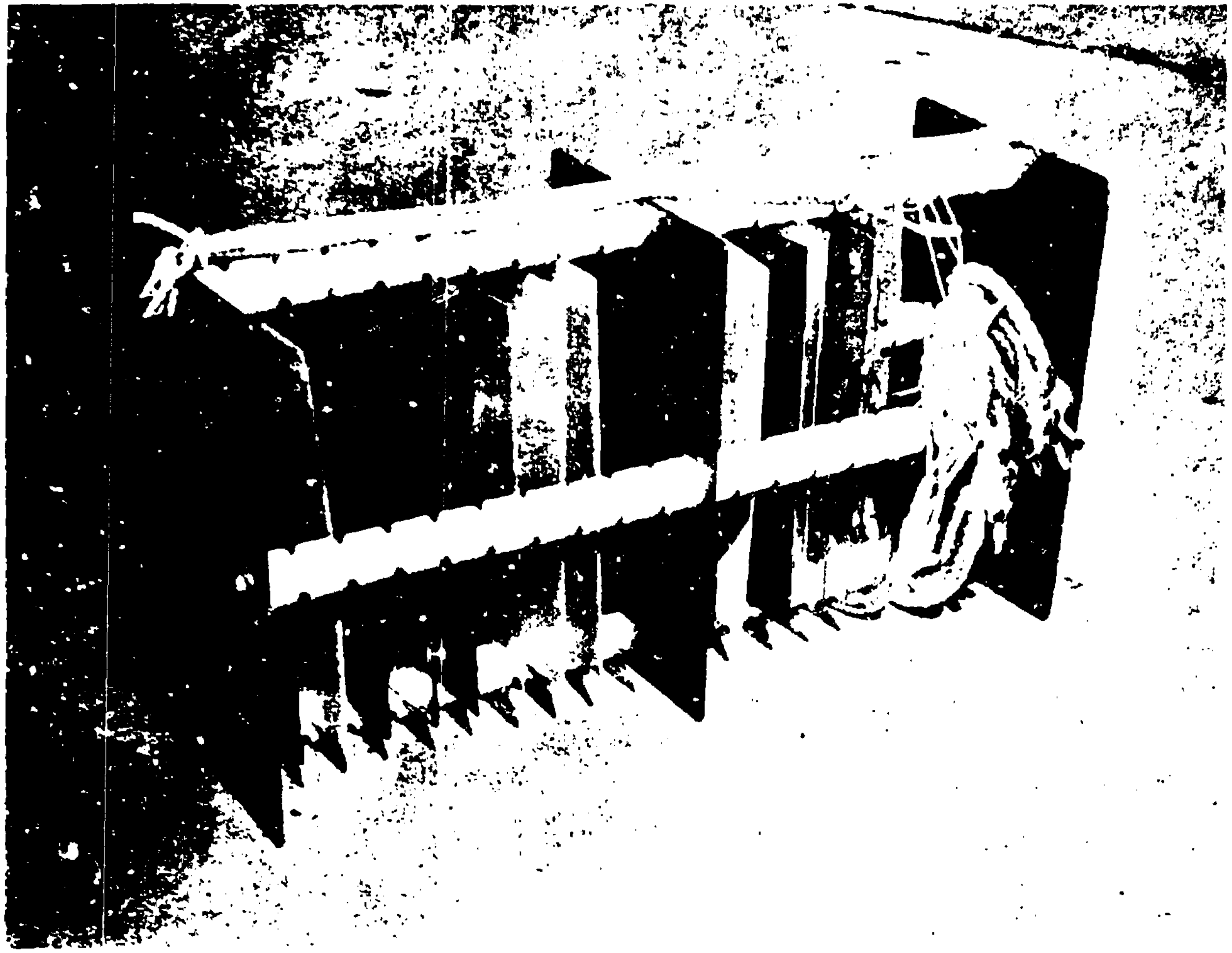

Figure 1. Test specimens assembled in a titanium rack for exposure in bottom sediment.

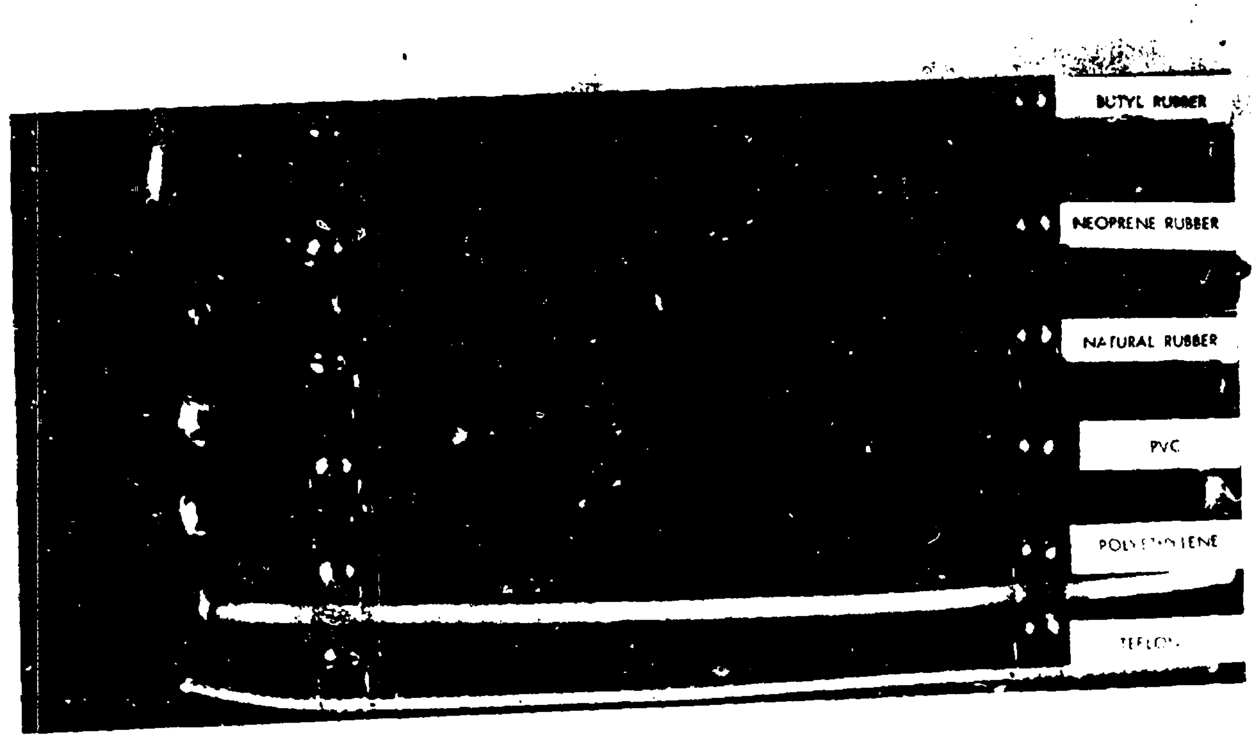

Figure 2. Various electrical cable insulation materials secured to a phenolic laminate plastic sheet.

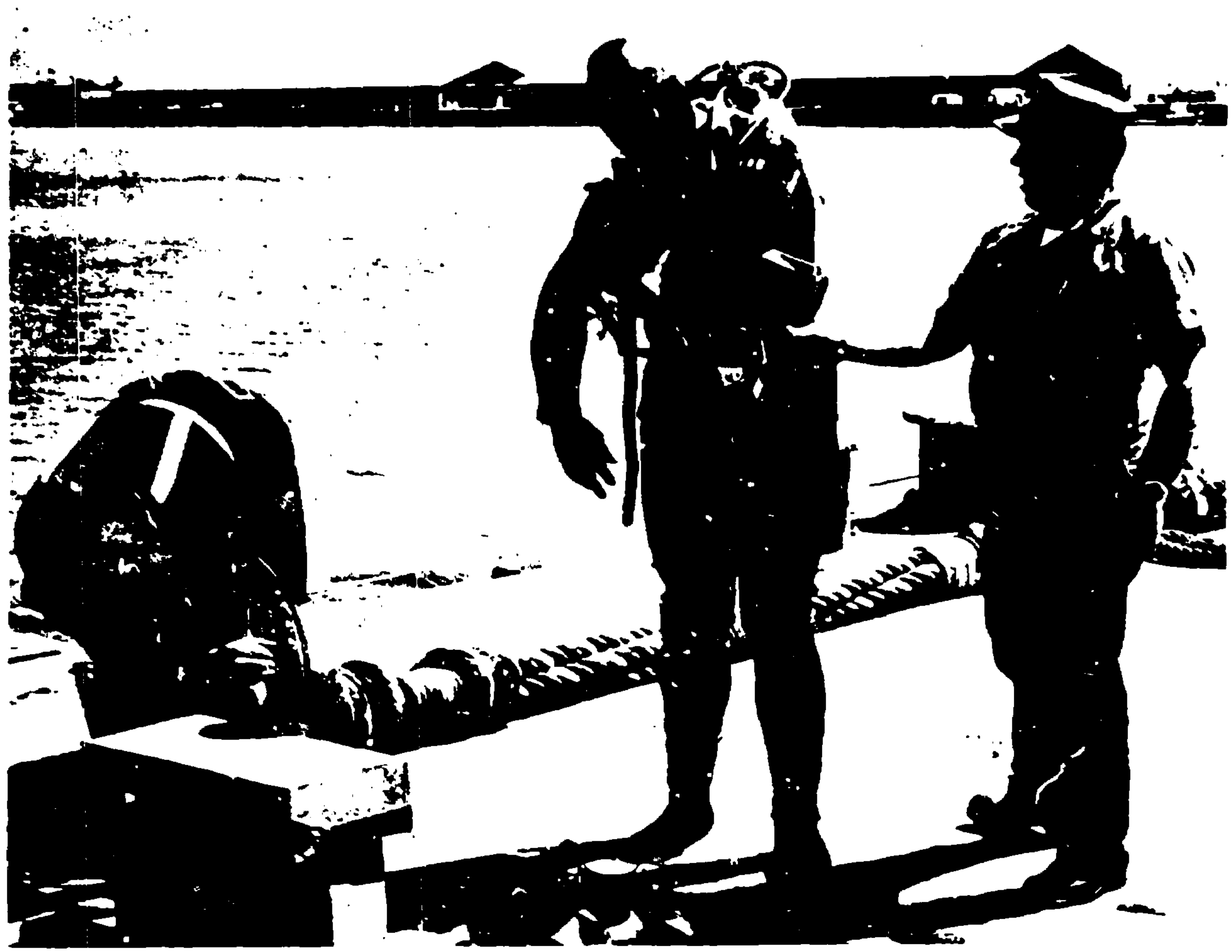

Figure 3. Scuba divers preparing to recover test specimens.

Figure 4. Titanium rack with materials recovered after one year exposed (partially) in bottom sediment of Port Hueneme Harbor.

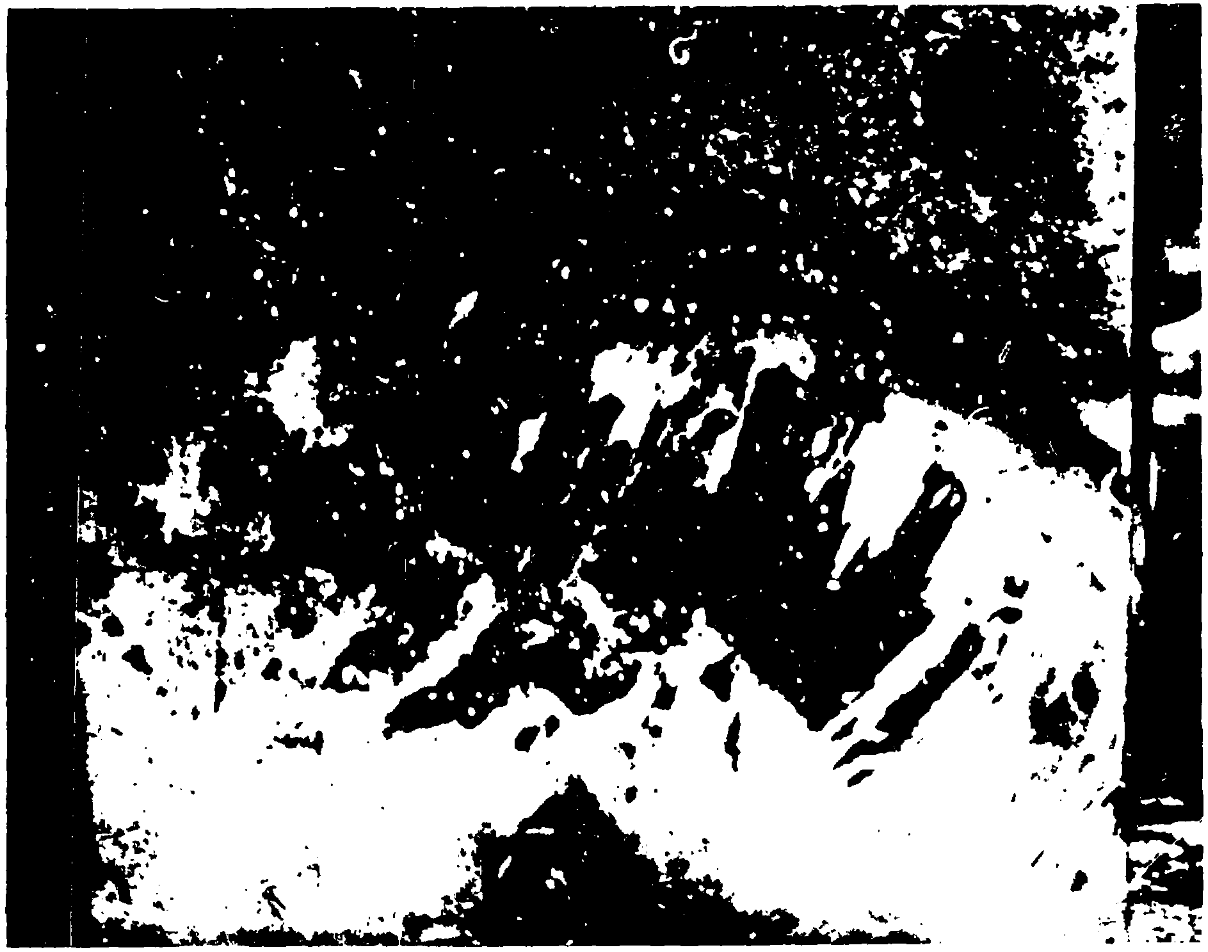

Figure 5. Black bottom mud attached to an end plate of a titanium rack when recovered.

Figure 6. Cotton rope (1/2 inch diameter) fibers decayed by marine microorganisms after one year exposure.

Figure 7. Manila rope (1/4 inch diameter) deteriorated by marine organisms after one year exposure.

Figure 8. Electrical cables recovered after one year exposure in bottom sediment of Port Hueneme Harbor.

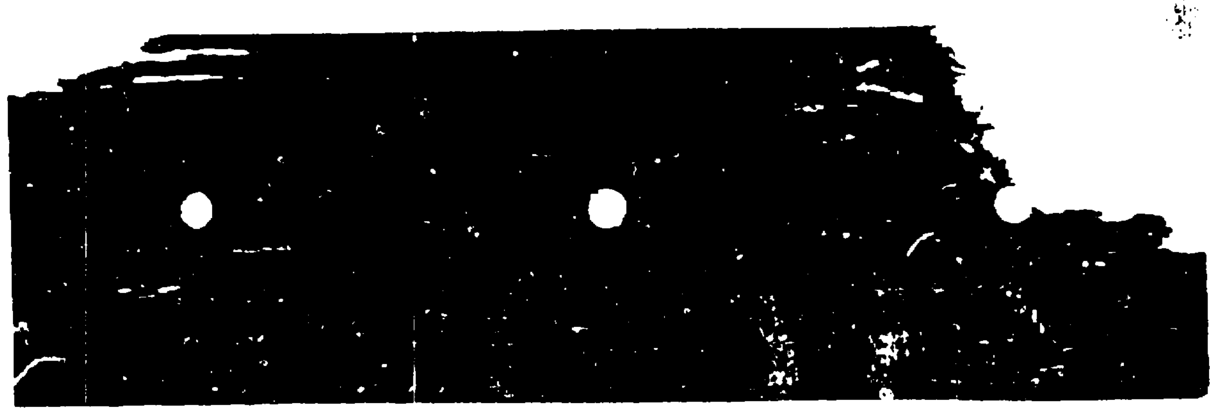

Figure 9. Douglas fir test panel deteriorated by molluscan and crustacean wood borers.

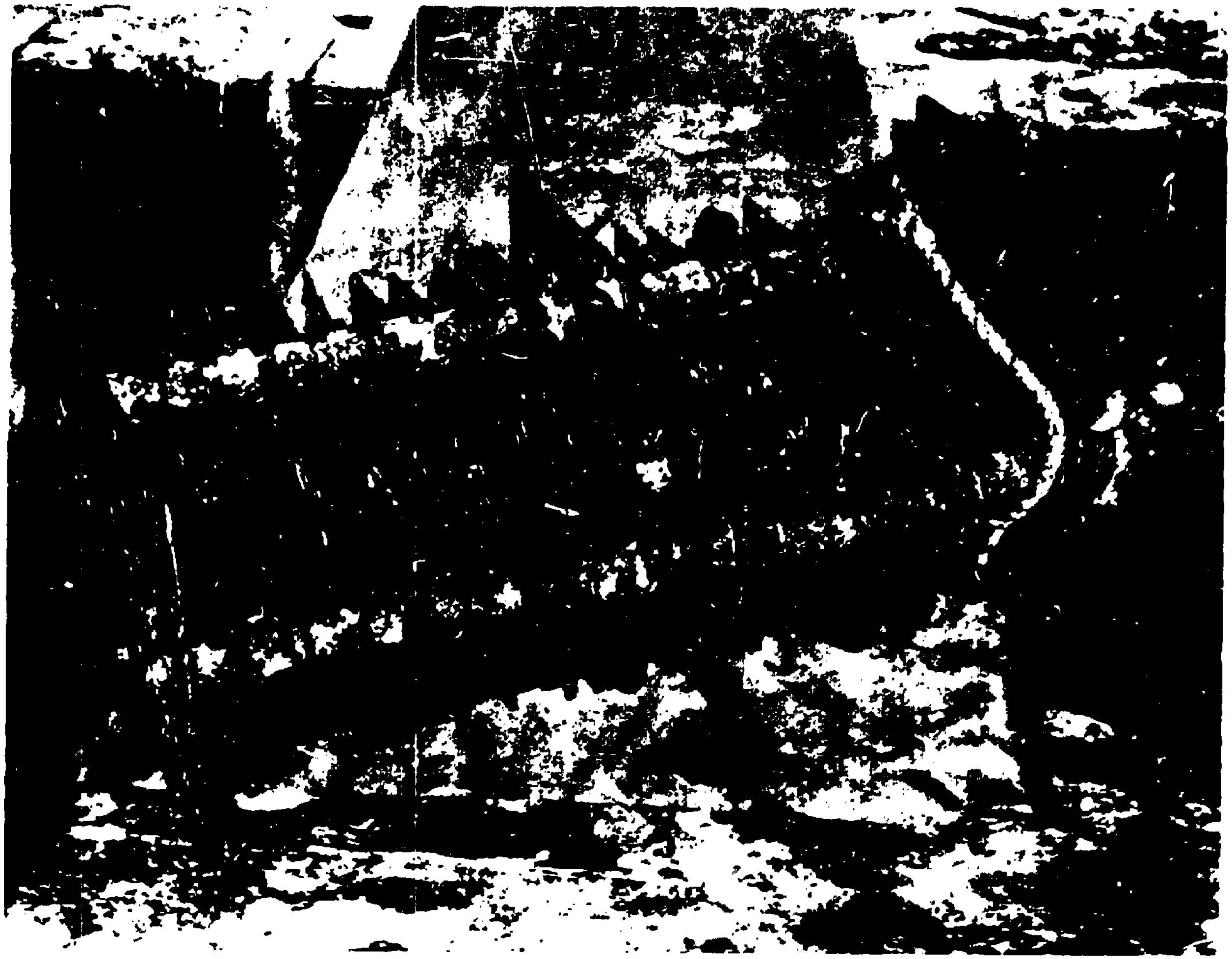

Figure 10. Replicate test specimens exposed at the surface of the water in Port Hueneme Harbor (one year).

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